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(54) SOLID ACTIVE CARBON

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a solid active carbon having a practical electrostatic capacity, excellent in mechanical strength and durability and suitable as various electrode materials, by constituting the active carbon so that the ratio of pore volume of a pore size not larger than a specific value to total pore volume is a specific ratio or above in pore distribution obtained from an argon adsorption isotherm and the capacitance is a specific value or above.

SOLUTION: This solid active carbon comprises active carbon powder or active carbon fiber or a mixture thereof and a carbonized product obtained by heat treating a carbonizable resin added as a binder. Pore volume of ≤ 15 \AA ; pore diameter in pore distribution of the solid-like active carbon obtained from an argon adsorption isotherm (HK) is $\geq 65\%$ based on total pore volume and electrostatic capacity in low electric current discharge of 30 mA/cm^2 is $\geq 20 \text{ F/cc}$. Palm shell-based active carbon is preferably used as the raw material and the specific surface area is selected according to the desired electrostatic capacity and an active carbon having $1500\text{-}2500 \text{ m}^2/\text{g}$ specific surface area is preferably used as a polarizing electrode for electric double layer capacitors and phenol or Teflon (R) is preferably used as the binder.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention An electric double layer capacitor and small mass capacitors including a lithium ion battery, It is related with the solid form active carbon generally widely applied as porous activated carbon used for the filtering media the electrode material used for various cells, such as a backup power supply, a power supply for vehicles, and auxiliary power, or gas adsorption material and the object for waterworks, the object for foodstuffs refining, for wastewater purification, etc.

[0002]

[Description of the Prior Art]In recent years, although application to the various applicable fields which paid their attention to the characteristic is considered, especially, activated carbon is taken up as a porous carbonaceous material a small mass capacitor and for the electrode materials of various cells, and is examined variously.

[0003]The polarizable electrode which makes carbonaceous of this activated carbon a subject, . Used the electric double layer which makes contain an electrolyte and is formed by both interface between these polarizable electrodes. It is used abundantly as an object for electric double layer capacitors which has the electric capacity which attains to one 1000 times the number per unit volume of this as compared with the conventional capacitor, This electric double layer capacitor is developing the demand quickly with development of the electronics field, such as being applied to auxiliary power, such as a small memory backup power supply and a mass motor, from having a function of both a capacitor and a cell.

[0004]As said electrode material, the solid form active carbon of the porosity generally applied widely is used, and at the beginning as such solid form active carbon, For example, what kneaded carbonaceous, such as activated carbon and carbon black, and organic resin, such as a fluorine polymer, and was fabricated by publicly known molding means, such as roll diffusion bonding, to the sheet shaped was used.

[0005]However, as an electrode material of a capacitor or a cell, In order to satisfy the

performance of especially high electric capacity and low internal resistance and to satisfy the demand of a miniaturization of the electronic parts of these days, To excel in nearby endurance and a mechanical property as a general object for filtering media with it being hard to cause a crack, breakage, etc. with the porous body structure in consideration of the minimization of volume to prescribed capacity and the impregnating ability of the electrolysis solution etc. is demanded.

[0006]Although especially the electric capacity of an electric double layer capacitor is governed by surface area of a polarizable electrode, electric capacity per unit volume, resistance of an electrode, etc. in which an electric double layer is formed, there are the size and relation of ion in the electrolysis solution which forms an electric double layer, and the specific surface area of micropore is considered to influence electric capacity.

[0007]Therefore, since the electric capacity per electrode unit volume was increased, it was needed that it is activated carbon of the porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength.

[0008]Then, in order to satisfy said many demands, mix and carry out pressure sintering of active carbon particles, the carbon fiber, etc., or. Or carry out injection molding of the mixture of activated carbon powder and powdered phenol resin, and heat-treat it, or, Or the prepreg sheet which adds a pulp fiber etc. to an activated carbon fiber, and mills paper, or uses activated carbon powder, a cellulose fiber, etc. as the main ingredients is stuck by pressure, Calcinate or the mixture of activated carbon powder and phenol resin is formed in the shape of a substrate, Heat cure of the mixture of the spheroidal carbide and thermal reaction type spherical phenol resin which heat-treated in the non-oxidizing atmosphere, or carbonized hardened type spherical phenol resin, and were obtained is carried out, Subsequently, after heat-treating by an inert atmosphere, the various solid form active carbon by various processes, such as carrying out activation treatment, is proposed (refer to JP,8-119614,A, JP,6-69075,A, JP,5-129157,A, and JP,3-201516,A).

[0009]

[Problem(s) to be Solved by the Invention]However, when said solid state activated carbon measures the electric capacity by a constant-current-discharge method, When it was lower than the electric capacity predicted from the rate of activated carbon and various organic resin or having been discharged by the low current about 30 mA/cm^2 , only 20 or less F/cc of electric capacity were obtained, but there was a technical problem were inapplicable in the electrode material of the electric double layer capacitor which needs high electric capacity.

[0010]

[Objects of the Invention]Accomplished this invention as a dissolution plug and said technical problem the purpose, The electric capacity predicted from the rate of activated carbon and various organic resin is fully pulled out, It has practical electric capacity and is in obtaining solid

form active carbon applicable to the various application which was moreover excellent in endurance with a large mechanical strength, and solid form active carbon especially suitable as an electrode material of an electric double layer capacitor or the various cells for auxiliary power.

[0011]

[Means for Solving the Problem] This invention persons fabricate wholeheartedly a mixture which comprises various activated carbon materials and carbonization nature resin of porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength to said technical problem as a result of research, By carrying out the carbonization unification of this Plastic solid in a non-oxidizing atmosphere, and controlling pore distribution of solid form active carbon, electric capacity at the time of low current discharge was high, and it had practical electric capacity, and found out that solid form active carbon excellent in a mechanical strength and endurance was obtained.

[0012] Namely, in pore distribution measurement which asks for solid form active carbon of this invention from argon adsorption isotherm by the Horvath-Kawazoe method (it is hereafter written as the HK method), When capacity with a pole diameter of 15A or less occupies not less than 65% of whole pore volume and measures the electric capacity by a constant-current-discharge method of 30 mA/cm², cc is shown in 20 or more F /.

[0013] Said solid form active carbon is the optimal also as a polarizable electrode of an electric double layer capacitor.

[0014]

[Function] Capacity with a pole diameter [in the pore distribution which asks for the solid form active carbon of this invention from argon adsorption isotherm] of 15A or less is not less than 65% of whole pore volume, And from the electric capacity measured by the constant-current-discharge method of 30 mA/cm² being 20 or more F/cc. There are many portions to which the trap of the sulfate ion in an electrolysis solution is carried out, and, moreover, 15 A is a size moderate although a trap is efficiently carried out from the size of said sulfate ion being about 3A.

It can be considered as the multiple-purpose solid form active carbon which was considered to have high electric capacity and was excellent in the mechanical strength and endurance with large electric capacity at the time of low current discharge as a result.

[0015] On the other hand, when said solid form active carbon is used as the polarizable electrode of an electric double layer capacitor, the ratio of activated carbon becomes large and the small electric double layer capacitor has practical electric capacity and the inner electrical resistance of the electrode excelled [electric double layer capacitor] in efficient endurance with an easy low structure is obtained.

[0016]

[Embodiment of the Invention] Hereafter, the solid form active carbon of this invention is explained in full detail. The solid form active carbon of this invention is what comprises activated carbon powder, an activated carbon fiber or activated carbon powder and an activated carbon fiber, and the carbide that heat-treated the publicly known carbonization nature resin added as a binder, When pore volume with a pole diameter [in the pore distribution of the solid form active carbon for which it asked from argon adsorption isotherm (the HK method)] of 15A or less is less than 65% of whole pore volume, Or when the electric capacity at the time of low current discharge of 30 mA/cm^2 is less than 20 F/cc, it becomes unsuitable as a polarizable electrode of an electric double layer capacitor.

[0017] Therefore, it is needed that pore volume with a pole diameter [in the pore distribution of the solid form active carbon for which it asked from argon adsorption isotherm (the HK method)] of 15A or less is not less than 65% of whole pore volume, and the electric capacity at the time of low current discharge of 30 mA/cm^2 is 20 or more F/cc.

[0018] In the solid form active carbon of this invention, in particular said activated carbon powder or the activated carbon fiber that are raw materials may not be limited, any, such as a coconut husks system, a Carboniferous system, a woody system, may be sufficient as them, and their coconut husks system is the most desirable in respect of cost and adsorption capability.

[0019] The activated carbon powder of said raw material should just choose the specific surface area with the target electric capacity, That whose specific surface area is $1500\text{--}2500 \text{ m}^2/\text{g}$ when using for the polarizable electrode for electric double layer capacitors especially is preferred, and when using an activated carbon fiber, that whose specific surface area a fiber diameter is $1000\text{--}2500 \text{ m}^2/\text{g}$ in 6-18 micrometers is preferred.

[0020] If the carbonization nature resin added as a binder is publicly known organic nature resin, it can apply either and is not limited in particular, but from a point of a moldability or the intensity of the solid form active carbon obtained, phenol or Teflon, coal tar, a polyvinyl butyral, etc. are preferred for it.

[0021] Next, an example of the manufacturing method of the solid form active carbon of this invention is described. To activated carbon powder and/or activated carbon fiber 100 weight section, phenol or Teflon, publicly known carbonization nature resin, such as coal tar and a polyvinyl butyral (PVB), -- at least a kind at a rate of 20 to 200 weight section, [mix and] A doctor blade method and a tape-forming method after preparing slurry or a granulated body from this mixture and producing the charge of shaping material, Or in advance of carbonization heat treatment, aging processing is performed for the Plastic solid fabricated by the molding method with publicly known compression moulding technique, roll diffusion bonding, or

molding method that combined them etc. at the temperature of 150-300 ** among the atmosphere.

[0022]Carbonization nature resin can hold the intensity of solid form active carbon highly in a small quantity, and the fine pores of activated carbon itself are made hard to plug up, and this aging processing does not reduce the surface area, but can pull out the characteristic of activated carbon to the maximum extent.

[0023]Subsequently, carry out carbonization heat treatment in a non-oxidizing atmosphere, and carbonization nature resin in a Plastic solid is carbonized, and the calcination unification of said activated carbon powder and/or an activated carbon fiber, and the carbide of carbonization nature resin is carried out, and solid form active carbon is obtained.

[0024]In order to advance sintering of the neck part of activated carbon powder or an activated carbon fiber and to make sufficient intensity hold, its temperature of 800-1200 ** is desirable, and its temperature which is 800-1000 ** is especially the optimal while said carbonization heat treatment temperature fully advances carbonization of carbonization nature resin.

[0025]If said carbonization treatment makes temperature high or carbonization time is lengthened, although intensity will improve, since it becomes the fall of whole pore volume and the electric capacity at the time of low current discharge falls, It is important to choose carbonization treatment conditions so that it may double with a use and may have suitable pore distribution from balance in intensity and electric capacity.

[0026]Fabricate the solid form active carbon of this invention to a sheet shaped by doctor blade method, the calendering roll method, etc., and consider it as activated carbon boards, or, It can be considered as various shape, and combining them. [fabricating by various press-forming methods to block like shape] [considering it as rod form or tubed by an extrusion method]

[0027]By heat-treating under a non-oxidizing atmosphere being also possible, and laminating and bonding two or more sheet-shaped Plastic solids by thermo-compression, or joining with adhesion liquid, adhesives, etc., after carrying out the plural laminates of said sheet-shaped Plastic solid, It also becomes possible to offset the mutual direction of curvature and to reduce generating of the curvature at the time of heat treatment.

[0028]

[Example]The solid form active carbon of this invention was evaluated as follows. First, a BET value receives coconut-shell-activated-charcoal powder 100 weight section of $1000\text{m}^2/\text{g}$, $1500\text{m}^2/\text{g}$, and $2000\text{m}^2/\text{g}$, The screen exception carried out the granular material obtained by preparing 100 weight sections and mesophase so that it may become 20 weight sections, and agitating PVB with a high-speed agitation mix machine with the sieve of 40 meshes, and the raw material for shaping was produced.

[0029]Next, press forming or after carrying out roll forming and acquiring a plate-like Plastic

solid, hold this Plastic solid for the obtained raw material for shaping at the inside of the atmosphere, and the temperature of 200 ** for 48 hours, and perform aging processing, and it ranks second, Carbonization heat treatment was performed among the vacuum by each temperature and retention time which are shown in Table 1, PVB and mesophase were carbonized and the activated carbon boards for evaluation (70 mm long which are a complex of activated carbon and carbon, the side of 50 mm, and 1 mm in thickness) were produced.

[0030]About the activated carbon boards for evaluation obtained in this way, pore distribution was measured from the argon adsorption isotherm (the HK method) which used the product ASAPPU made from Shimazu-micro MERITIKKUSU 2010M type, and the pore diameter searched for the rate with a pore volume of 15A or less.

[0031]The pore distribution searched for from the argon adsorption isothermal curve of the sample number 2 which is typical solid form active carbon of this invention is shown in drawing 1.

[0032]The activated carbon boards for evaluation were used as the electrode of an electric double layer capacitor, and among 40% of the weight of sulfuric acid solution, after charging for 30 minutes on the voltage of 0.9V, the electric capacity per electrode unit volume (F/cc) was calculated by the constant-current-discharge method of 30 mA/cm².

[0033]On the other hand, according to JIS-R-1601 standard, three point bending intensity was measured using the activated carbon boards for said evaluation.

[0034]

[Table 1]

試料 番号	活性炭 BET 値 (m^2/g)	炭 化 処 理		細孔容積 $\leq 15 \text{ \AA}$ (%)	静 電 容 客 量 (F/cc) (A)	曲 げ 強 度 (g/mm^2)	備 考
		温 度 ($^{\circ}\text{C}$)	時 間 (min)				
* 1	2000	700	240	88.0	—	108	測定不可
2	"	800	10	85.3	40.0	382	
3	"	"	30	80.1	34.1	391	
4	"	"	60	75.8	29.6	401	
5	"	"	120	73.6	27.5	412	
6	"	"	240	73.1	27.0	422	
7	"	900	10	81.5	35.6	509	
8	"	"	30	76.3	30.1	521	
9	"	"	60	71.8	25.8	535	
10	"	"	120	69.5	23.7	549	
11	"	"	240	67.9	22.4	563	
12	"	1000	10	77.8	31.6	678	
13	"	"	30	72.6	26.5	685	
14	"	"	60	67.7	22.2	713	
15	"	"	120	65.5	20.4	732	
* 16	"	"	240	63.7	19.0	751	
17	"	1100	10	73.8	27.6	905	
18	"	"	30	68.9	23.2	926	
* 19	"	"	120	62.5	18.1	977	
* 20	"	"	240	60.7	16.8	1001	
21	"	1200	10	69.9	24.1	1206	
22	"	"	30	65.3	20.2	1236	
* 23	"	"	60	60.6	16.7	1268	
* 24	"	1300	10	64.5	19.6	889	
25	1500	800	"	72.5	26.4	458	
26	"	"	30	68.1	22.5	469	
27	"	900	10	69.3	23.5	611	
* 28	"	"	30	64.9	19.9	506	
29	"	1000	10	66.1	20.9	814	
* 30	"	"	30	61.7	17.5	834	
* 31	"	1100	10	62.7	18.3	1085	
32	1000	800	"	65.5	20.4	649	

*印を付した試料番号は本発明の請求範囲外のものである。

[0035]As shown in a table, the sample number 1 which is outside the generic claim of this invention, To whole pore volume, although the pore volume of 15A or less is not less than 65%, Measurement of electric capacity cannot be performed at the time of low current discharge of $30 \text{ mA}/\text{cm}^2$, And with $108 \text{ g}/[\text{mm}]^2$, flexural strength is also low and, similarly in the sample numbers 16, 19, 20, 23, 24, 28, 30, and 31. The pore volume of 15A or less will be less than 65% to whole pore volume, and its electric capacity at the time of low current discharge of $30 \text{ mA}/[\text{cm}]^2$ is also low in 20 or less F/[cc and], To being unsuitable as multiple-purpose solid form active carbon including the polarizable electrode of an electric double layer capacitor, by this invention, the electric capacity at the time of said low current discharge is all large enough, and flexural strength also shows more than $382 \text{ g}/[\text{mm}]^2$.

[0036]

[Effect of the Invention]As explained in full detail above, according to the solid form active carbon of this invention, the electric capacity measured by the constant-current-discharge method of 30 mA/cm^2 is large, Solid form active carbon with the flexibility excellent in endurance with a large mechanical strength is obtained, When it is especially suitable as an electrode material of an electric double layer capacitor or the various cells for auxiliary power and the solid form active carbon of this invention is used as a polarizable electrode, The surface area which touches an electrolysis solution as an electrode increases, and since the cable run which an electric charge passes also increases, the small electric double layer capacitor which was excellent in efficient endurance with an easy structure of having practical electric capacity can be obtained.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]Solid form active carbon, wherein electric capacity which pore volume of 15A or less is not less than 65% of whole pore volume, and a pole diameter measured by a constant-current-discharge method of $30\text{mA}/[\text{cm}]^2$ in pore distribution searched for from argon adsorption isotherm is 20 or more F/cc.

[Claim 2]The solid form active carbon according to claim 1 using said solid form active carbon as a polarizable electrode of an electric double layer capacitor.

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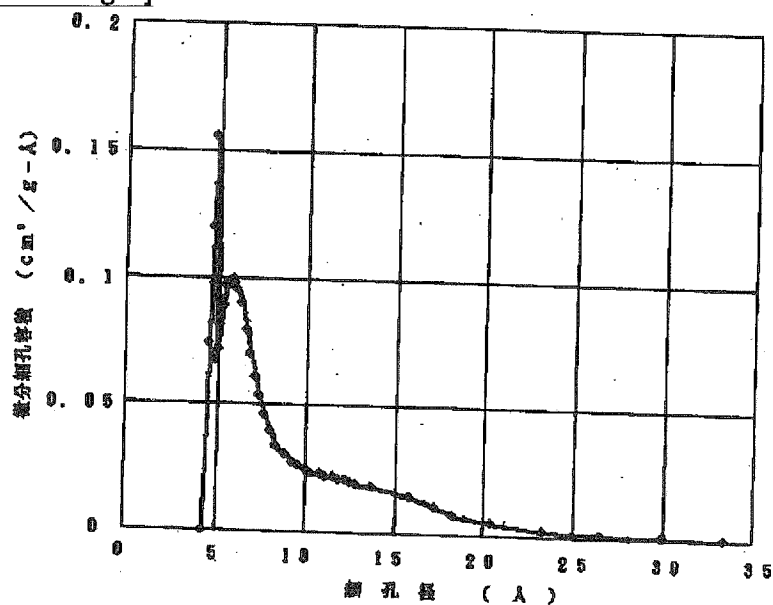
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DRAWINGS

[Drawing 1]



[Translation done.]

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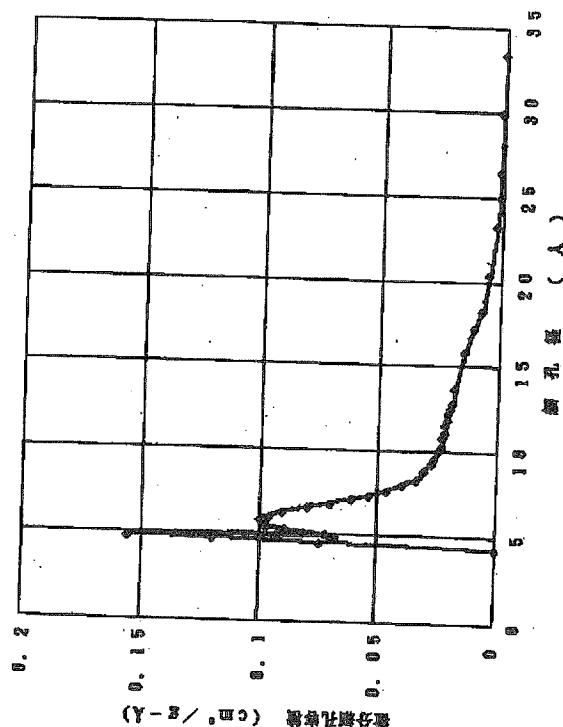
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(54)【発明の名称】 固形状活性炭

(57)【要約】

【課題】活性炭と各種有機樹脂との割合から予測される静電容量を十分に引き出し、実用的な静電容量を有し、かつ機械的強度の大きい耐久性に優れた汎用性のある固形状活性炭、とりわけ電気二重層コンデンサや補助電源用各種電池の電極材料として好適な固形状活性炭を得る。

【解決手段】アルゴン吸着等温線(HK法)から求めた固形状活性炭の細孔分布における15Å以下の細孔径の細孔容積は全細孔容積の65%以上で、かつ30mA/cm²の低電流放電時の静電容量が20F/cc以上である固形状活性炭。



【特許請求の範囲】

【請求項1】アルゴン吸着等温線から求める細孔分布において、細孔径が15Å以下の細孔容積が全細孔容積の65%以上であり、かつ30mA/cm²の定電流放電法で測定した静電容量が20F/cc以上であることを特徴とする固形状活性炭。

【請求項2】前記固形状活性炭を電気二重層コンデンサの分極性電極としたことを特徴とする請求項1記載の固形状活性炭。

【発明の詳細な説明】**【0001】**

【発明の属する技術分野】本発明は、電気二重層コンデンサやリチウムイオン電池をはじめとする小型大容量のコンデンサや、バックアップ電源、車両用電源、補助電源等の各種電池に用いられる電極材料、あるいはガス吸着材や上水用、食品精製用、排水浄化用等の濾材に用いられる多孔質の活性炭として一般に広く適用される固形状活性炭に関するものである。

【0002】

【従来の技術】近年、活性炭はその特性に着目した各種応用分野への適用が検討されているが、特に小型大容量のコンデンサや、各種電池の電極材料用の多孔性炭素材として取り上げられ、種々検討されている。

【0003】かかる活性炭等の炭素質を主体とする分極性電極は、該分極性電極間に電解質を含有させ、両者の界面で形成される電気二重層を利用した、従来のコンデンサに比較して単位体積当たり数千倍にも及ぶ静電容量を有する電気二重層コンデンサ用として多用され、かかる電気二重層コンデンサはコンデンサと電池の両方の機能を有することから、小型のメモリーバックアップ電源や大容量のモーター等の補助電源に適用される等、エレクトロニクス分野の発展と共に急速にその需要を伸ばしている。

【0004】当初、前記電極材料としては、一般に広く適用される多孔質の固形状活性炭が用いられており、そのような固形状活性炭としては、例えば、活性炭やカーボンブラック等の炭素質と、含フッ素重合体等の有機樹脂を混練してロール成形法等の公知の成形手段でシート状に成形したもの等が用いられていた。

【0005】しかしながら、コンデンサや電池の電極材料としては、とりわけ高い静電容量と低い内部抵抗という性能を満足し、かつ昨今の電子部品の小型化の要求を満足するために、所定容量に対する体積の極小化、及び電解液の含浸性を考慮した多孔体構造で亀裂や破損等を起こし難いことと共に、一般の濾材用としてもより耐久性と機械的特性に優れたものであること等が要求されるようになっていた。

【0006】特に、電気二重層コンデンサの静電容量は、電気二重層が形成される分極性電極の表面積や単位体積当たりの静電容量、電極の抵抗等にも配されるが

電気二重層を形成する電解液中のイオンの大きさと関係があり、微細孔の比表面積が静電容量を左右すると考えられている。

【0007】従って、電極単位体積当たりの静電容量を増すために、耐久性や機械的強度を損なわない範囲で比表面積を大きくした多孔質の活性炭であることが必要とされていた。

【0008】そこで、前記諸要求を満足するために、活性炭微粒子やカーボン繊維等を混合して加圧焼結したり、あるいは活性炭粉末と粉末状フェノール樹脂の混合物を射出成形して熱処理したり、あるいは活性炭繊維にパルプ繊維等を加えて抄造したり、あるいは活性炭粉末とセルロース繊維等を主成分とするブリプレグシートを圧着、焼成したり、又は活性炭粉末とフェノール樹脂の混合物を基板状に成膜し、非酸化性雰囲気中で熱処理を行ったり、あるいは硬化型球状フェノール樹脂を炭化して得た球状炭化物と熱反応型球状フェノール樹脂との混合物を加熱硬化し、次いで不活性雰囲気中で熱処理した後、賦活処理する等、種々の製法による各種固形状活性炭が提案されている（特開平8-119614号公報、特開平6-69075号公報、特開平5-129157号公報、特開平3-201516号公報参照）。

【0009】

【発明が解決しようとする課題】しかしながら、前記固形状活性炭は、その静電容量を定電流放電法で測定した場合、活性炭と各種有機樹脂との割合から予測される静電容量より低かったり、30mA/cm²程度の低電流で放電すると20F/cc以下の静電容量しか得られず、高い静電容量が必要な電気二重層コンデンサの電極材料には適用できないという課題があった。

【0010】

【発明の目的】本発明は、前記課題を解消せんとして成されたもので、その目的は、活性炭と各種有機樹脂との割合から予測される静電容量を十分に引き出し、実用的な静電容量を有し、しかも機械的強度の大きい耐久性に優れた各種用途に適用可能な固形状活性炭、とりわけ電気二重層コンデンサや補助電源用各種電池の電極材料として好適な固形状活性炭を得ることにある。

【0011】

【課題を解決するための手段】本発明者等は前記課題に対して鋭意研究の結果、耐久性や機械的強度を損なわない範囲で比表面積を大きくした多孔質の各種活性炭材料と炭化性樹脂から成る混合物を成形し、該成形体を非酸化性雰囲気中で炭化一体化して固形状活性炭の細孔分布を制御することにより、低電流放電時の静電容量が高く、実用的な静電容量を有すると共に、機械的強度と耐久性に優れた固形状活性炭が得られることを見いだした。

【0012】即ち、本発明の固形状活性炭は、Horvath-Kawazoe法（以下HK法と略記する）

によるアルゴン吸着等温線から求める細孔分布測定において、15 Å以下の細孔径の容積が全細孔容積の65%以上を占め、かつその静電容量を30 mA/cm²の定電流放電法で測定した時、20 F/cc以上を示すことを特徴とするものである。

【0013】また、前記固形状活性炭は電気二重層コンデンサの分極性電極としても最適なものである。

【0014】

【作用】本発明の固形状活性炭は、アルゴン吸着等温線から求める細孔分布における15 Å以下の細孔径の容積が全細孔容積の65%以上で、かつ30 mA/cm²の定電流放電法で測定した静電容量が20 F/cc以上であることから、電解液中の硫酸イオンがトラップされる部分が多く、しかも、15 Åというのは、前記硫酸イオンの大きさが約3 Åであることから、効率よくトラップするのに適度な大きさであり、高い静電容量を有すると考えられ、その結果、低電流放電時の静電容量が大きい、機械的強度及び耐久性に優れた多目的の固形状活性炭とすることができる。

【0015】一方、前記固形状活性炭を電気二重層コンデンサの分極性電極とした場合、活性炭の比率が大きくなり実用的な静電容量を有し、かつ電極の内部電気抵抗が低い、簡単な構造で効率の良い、耐久性に優れた小型の電気二重層コンデンサが得られる。

【0016】

【発明の実施の形態】以下、本発明の固形状活性炭について詳述する。本発明の固形状活性炭は、活性炭粉末又は活性炭繊維、あるいは活性炭粉末及び活性炭繊維と、バインダーとして添加される公知の炭化性樹脂を熱処理した炭化物とから成るもので、アルゴン吸着等温線(HK法)から求めた固形状活性炭の細孔分布における15 Å以下の細孔径の細孔容積が全細孔容積の65%未満の場合、あるいは30 mA/cm²の低電流放電時の静電容量が20 F/cc未満の場合には、電気二重層コンデンサの分極性電極としては不適当となる。

【0017】従って、アルゴン吸着等温線(HK法)から求めた固形状活性炭の細孔分布における15 Å以下の細孔径の細孔容積は全細孔容積の65%以上で、かつ30 mA/cm²の低電流放電時の静電容量が20 F/cc以上であることが必要となる。

【0018】本発明の固形状活性炭において、原料である前記活性炭粉末や活性炭繊維は特に限定するものではなく、ヤシ殻系や石炭系、木質系等のいずれでも良く、コストと吸着能力の点ではヤシ殻系が最も望ましい。

【0019】尚、前記原料の活性炭粉末は目的とする静電容量によってその比表面積を選択すれば良く、特に電気二重層コンデンサ用の分極性電極に用いる場合には比表面積が1500~2500 m²/gであるものが好適であり、活性炭繊維を用いる場合には、繊維径が6~18 μmで比表面積が1000~2500 m²/gである

ものが好適である。

【0020】また、バインダーとして添加される炭化性樹脂は、公知の有機性樹脂であればいずれでも適用でき、特に限定するものではないが、成形性あるいは得られる固形状活性炭の強度の点からは、フェノール又はテフロン、コールタール、ポリビニルブチラール等が好適である。

【0021】次に、本発明の固形状活性炭の製造方法の一例を述べる。活性炭粉末及び/又は活性炭繊維100重量部に対して、フェノール又はテフロン、コールタール、ポリビニルブチラール(PVB)等、公知の炭化性樹脂の少なくとも一種を20~200重量部の割合で混合し、該混合物から泥漿又は造粒体を調製して成形用材料を作製した後、ドクターブレード法やテープ成形法、又は加圧成形法やロール成形法、あるいはそれらを組み合わせた成形法等の公知の成形法で成形した成形体を炭化熱処理に先立ち、大気中、150~300℃の温度でエージング処理を行う。

【0022】かかるエージング処理は、炭化性樹脂が少量で固形状活性炭の強度を高く保持することができると共に、活性炭自体の細孔を塞ぎ難くしてその表面積を低減せず、活性炭の特性を最大限に引き出せる。

【0023】次いで、非酸化性雰囲気中で炭化熱処理し、成形体中の炭化性樹脂を炭化すると共に、前記活性炭粉末及び/又は活性炭繊維と炭化性樹脂の炭化物とを焼成一体化して固形状活性炭を得る。

【0024】前記炭化熱処理温度は、炭化性樹脂の炭化を十分に進行させるとともに、活性炭粉末や活性炭繊維のネック部の焼結を進行させて十分な強度を保持させるためには800~1200℃の温度が望ましく、特に800~1000℃の温度が最適である。

【0025】また、前記炭化処理は温度を高くしたり、炭化時間を長くすれば強度は向上するものの、全細孔容積の低下となり、低電流放電時の静電容量が低下してしまうため、用途に合わせ強度と静電容量に兼ね合いから、好適な細孔分布を有するように炭化処理条件を選択することが肝要である。

【0026】なお、本発明の固形状活性炭は、ドクターブレード法やカレンダーロール法等によりシート状に成形して活性炭基板としたり、各種プレス成形法でブロック状に成形したり、あるいは押出成形法により棒状や筒状としたり、それらを組み合わせたりしてさまざまな形状とすることができる。

【0027】更に、前記シート状成形体を複数積層した後、非酸化性雰囲気下で熱処理することも可能であり、複数のシート状成形体を積層し、熱圧着したり、あるいは密着液や接着剤等で接合することにより、互いの反り方向を相殺して熱処理時の反りの発生を低減することも可能となる。

【0028】